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METHOD OF PREPARING FUEL FORMULATIONS ALLOWING OPTIMAL OPERATION OF AN ENGINE DEVELOPED FOR THE HCCI COMBUSTION MODE

In order to prepare fuel formulations allowing optimal operation of an internal combustion engine developed for the HCCI combustion mode, a method is described which employs:

- a fuel base comprising a Jet B; and
- possibly a component or combination of components, the nature and the proportions of which are selected so as to provide the mixture with a distillation curve, the course of which is representative of that of a petroleum product (monotonous curve), in particular of a fuel for diesel engines having optimal properties for low speeds-low loads as well as for high speeds-high loads.

Formulations prepared according to this method are described.

The invention relates to fuel formulations, the composition of which is optimised for operation according to the HCCI combustion mode. It relates also to a method for preparing these formulations.

It is known that combustion by auto-ignition in the fairly homogenous phase (called "HCCI", from the English "Homogeneous Charge Compression Ignition") can be obtained both in diesel engine applications as well as in petrol engine applications. In both cases, the preparation of the fairly homogeneous air-fuel mixture required for the HCCI may be carried out either by pre-mixture in the admission or by direct injection of the fuel (or another air-fuel mixture) into the combustion chamber. The application of HCCI combustion to the diesel type engine presently relies on the pair engine/standard gas oil EN590. The entire relevance of the HCCI technology is based on the potential of operating in the homogeneous phase in the widest possible range of applications. The only presently feasible fuel within the scope of an application to a diesel engine is, in particular, the said gas oil EN590.

The combustion mode by auto-ignition under conditions of the air-fuel mixture which are, for the most part, homogeneous, requires certain "fuel" qualities which are not offered by the conventional gas oil for a better utilisation. By way of example the distillation curve of the gas oil EN590 is cited, which does not permit an optimal operation in the homogeneous mode. Also, the delay of auto-ignition of standard gas oils might not be adapted when used at a low load while being satisfactory for high loads. It therefore appears to be obvious that the available gas oil EN590 does not permit an optimal range of application of the HCCI combustion mode.

It is the object of this invention to permit use in the HCCI combustion mode under the best possible conditions and across the widest possible range of speed/load by proposing a new fuel adapted to this use.

To permit operation in the HCCI mode on the widest possible scale:

- vaporisation of the fuel must be well controlled;
- the regulation of combustion initiation must be well controlled; and
- the sequence of combustion must be well controlled;

and this for the greatest diversity of operation conditions.

The fuel proposed to meet these requirements is formulated such that it meets different relevant criteria for the HCCI combustion mode. These are:

- having a volatility higher than that of a standard gas oil so as to ensure the existence of a homogeneous mixture as soon as possible; and
- having an auto-ignition delay controllable throughout the advantageously selected base product and throughout the wide incorporation of different compounds.

The formulations prepared according to the invention can be defined in that they include a major proportion of a jet fuel, called "Jet B" and a combination of components the nature and properties of which are advantageously so selected as to provide a distillation curve for the mixture, the course of which is representative of that of a petroleum product, in particular of a diesel engine fuel.

The "Jet B", forming the basis of these formulations, is defined in the ASTM D-1655 standard or in NATO's F45 standard. Having a wide cut (of about 70 to 200 or 250°C), it permits easier vaporisation.

In order to produce the fuel formulations according to the invention, a selection of products, chosen from a wide range of compounds is incorporated into this base, such as:

- paraffins, e.g. 2-methylhexane, n-heptane, 2-methyloctane, 2-methylnonane, n-octane, 3,6-dimethyloctane, 3-methylnonane, 2,9-

dimethyl-5,6-diisoamyldecane, nonane, decane, undecane, 3-ethyldecane, 5-butylnonane, 7,8-dimethyltetradecane, 2,6,10-trimethyldodecane, 2,3,10-trimethylundecane, 6-propyldodecane, linear paraffins C_nH_{2n+2} with $n \geq 14$;

- nitrated compounds, e.g. nitro methane, nitro ethane, nitro propane, nitrobenzene, nitro toluene;
- oxygenated compounds such as:
 - peroxides, e.g. tert-butyl peroxide;
 - carbonates, e.g. diethyl carbonate;
 - acetals, e.g. polyethoxyethylal;
 - ethers, e.g. dimethoxymethane, diethoxypropane, diethoxybutane, di-n-pentylether, di-n-pentoxymethane;
 - alcohols, e.g. octanol, nonanol, dodecanol;
 - glycol ethers, e.g. dimethylglycol, dimethyldiglycol, ethyldiglycol, ethyltriglycol; and
 - glycol esters, e.g. butyl glycol acetate. -

The incorporation rate of these products is generally from 0 to 50% by volume. They can be incorporated alone or as mixtures.

In order to be able to formulate a fuel capable of meeting this wide range of requirements, it is proposed to start from a petroleum fraction consisting of a "Jet B". This fraction will be called "B".

Moreover, in order to provide the elements meeting the three requirements mentioned above, the fuels are formulated by splitting up the space into a matrix arranged around the cetane number of chemical compounds and the distillation range of these compounds.

This matrix which will be called the matrix of auto-ignition delay (or MAID") presents itself in the following manner:

MAID

Cetane range	40-45 (I)	45-50 (II)	50-55 (III)	>55 (IV)
Distillation range (°C)				
50-100	1	2	3	4
100-150	5	6	7	8
150-200	9	10	11	12
200-250	13	14	16	17
>250	17	18	19	20

The compounds I, II, III and IV are products selected from different chemical families, defined further above.

Thus, taking into account their boiling point and their cetane number (Indicated in brackets behind each component) one considers:

- as component 1, e.g. 2-methylhexane (87°C, 40);
- as component 2, e.g. dimethylglycol (85°C, 53) and n-heptane (98°C, 56);
- as component 3, e.g. dimethoxymethane (42°C, 52);
- as component 4, e.g. nitro methane (100°C, >100);
- as component 5, e.g. diethyl carbonate (127°C, 40) or 2-methylheptane (135°C, 41);
- as component 6, e.g. 2-methyl octane (148°C, 49);
- as component 7, e.g. 2-methyl nonane (150°C, 54);
- as component 8, e.g. diethoxy propane (124°C, 136), diethoxy butane (145°C, 143), nitro ethane (115°C, > 100), nitro propane (120°C, >>100) or n-octane (126°C, 63);
- as component 9, e.g. octanol (196°C, 43), butyl glycol acetate (156°C, 41) or 3,6-dimethyl octane (166°C, 41);
- as component 10, e.g. 3-methyl nonane (185°C, 47);

- as component 11, e.g. 2,9-dimethyl-5,6-diisoamyl decane (154°C, 52);
- as component 12, e.g. di-n-pentyl ether (187°C, 109), dimethyl diglycol (162°C, >70), nonane (151°C, 68), decane (174°C, 76) or undecane (196°C, 77);
- as component 13, e.g. ethyl diglycol (202°C, 41);
- as component 14, e.g. 3-ethyl decane (202°C, 48);
- as component 15, e.g. 5-butyl nonane (213°C, 53);
- as component 16, e.g. nonanol (215°C, 60), di-n-pentoxymethane (218°C, 97), nitrobenzene (210°C >100) or nitro toluene (230°C, >>100);
- as component 17, e.g. 7,8-dimethyl tetradecane (269°C, 40) or 2,6,10 trimethyl dodecane (352°C, 41);
- as component 18, e.g. 2,3,10-trimethyl undecane (250°C, 47);
- as component 19, e.g. 6-propyl dodecane (250°C, 52); and
- as component 20, e.g. dodecanol (260°C, 68), ethyl triglycol (255°C, > 70), the linear paraffins C_nH_{2n+2} , $n \geq 14$) or polyethoxy ethylal (>200°C, 140).

In order to formulate a fuel according to the invention, a mixture is produced composed of a "Jet B" and of one or more elements taken in different concentrations from the above mentioned "MAID" matrix.

Therefore, a formulation of the invention may be represented by the formula:

$$B_{100-(a+b+c+d)}I_aII_bIII_cIV_d$$

representing a mixture composed of a % of the compound of column I, b % of the compound of column II, c % of the compound of column III and d % of the compound of column IV of the above MAID matrix.

A formulation presents itself, for example, in the form of a mixture of the formula:

$$B_{100-(a+b+c+d)}1_a6_b11_c16_d$$

representing a mixture composed of a % of the compound of the family 1, b % of the compound of the family 6, c % of the compound of the family 11 and d % of the compound of the family 16.

In a more specific manner, the components of the mixture are chosen, in appropriate proportions, substantially along the diagonal line extending from the top left towards the bottom right of the said "MAID" matrix. Preferably, the formulations are produced with a representative of each line in appropriate proportions to ensure a distillation curve representative of a petroleum product (monotonous curve).

Furthermore, a characterisation procedure for the engine operation in the homogeneous combustion mode has been developed. Coupling this procedure to the table of the auto-ignition delay ("MAID matrix), shown further above, allows proposing adapted fuel formulations. This coupling is shown in the diagram below.

Cetane range		40 - 45	45 - 50	50 - 55	> 55	
Distillation range (°C)		(I)	(II)	(III)	(IV)	
<i>S_LL_l</i>	50 - 100	1	2	3	4	<i>S_HL_l</i>
	100 - 150	5	6	7	8	
	150 - 200	9	10	11	12	
<i>S_LL_h</i>	200 - 250	13	14	15	16	<i>S_HL_h</i>
	> 250	17	18	19	20	

Engine speed →

↓ Load

The designation "S_xL_x" relates to the functioning point of the engine, the letters S and L respectively refer to engine speed (Speed) and the load (Load). Each of these letters is followed by a letter (h or l) indicating the high or low level of this parameter.

Thus, for a fuel intended for low speed/low load and high speed/high load operations, a formulation of the type B₃₀1₁₀5₁₀15₂₅20₂₅ will be adapted.

As other examples of formulations being of great interest as fuels for engines operating according to the HCCI mode, the following may be cited amongst many others:

- B₆₀1₅6₁₀10₁₀15₁₀20₅ and
- B₇₀1₁₀15₁₀20₁₀.

Furthermore, the promoter role of the mixtures considered in the invention for the homogeneous combustion HCCI may be enhanced by being coupled to the recirculation circuit of the exhaust gases (EGR).

CLAIMS

1. Method of preparing a fuel formulation for an internal combustion engine, characterised in that a composition is determined, characterised in that a fuel base among the Jets B is selected, such as defined by the ASTM D-1655 standard and by possibly incorporating therein at least one component or combination of components selected from:

- the paraffins;
- the nitrated compounds;
- the peroxides;
- the carbonates;
- the acetals;
- the ethers;
- the alcohols;
- the glycol ethers; and
- the glycol esters,

in a manner to provide a distillation curve for the mixture the course of which is representative of that of a fuel adapted to the requirements of the operation of engines in the HCCL combustion mode or combustion by auto-ignition in the fairly homogeneous phase.

2. Method according to claim 1, characterised in that the components to be added to the Jet B are selected from the matrix below:

Cetane range	40-45 (I)	45-50 (II)	50-55 (III)	>55 (IV)
Distillation range (°C)				
50-100	1	2	3	4
100-150	5	6	7	8
150-200	9	10	11	12
200-250	13	14	16	17
>250	17	18	19	20

wherein the numbers 1 to 20 each represent a family of compounds having a boiling temperature and a cetane number within the ranges indicated, the said components being chosen substantially along a diagonal direction extending from the top left towards the bottom right of the said matrix.

3. Method according to claim 2, characterised in that a formulation is produced by incorporating into the Jet B a representative of each line of the said matrix.

4. Method according to any one of claims 1 to 3, characterised in that the combination of compounds contains at least one compound selected from:

- 2-methylhexane, n-heptane, 2-methyloctane, 2-methylnonane, n-octane, 3,6-dimethyloctane, 3-methylnonane, 2,9-dimethyl-5,6-diisooamyldecane, nonane, decane, undecane, 3-ethyldecane, 5-butyl nonane, 7,8-dimethyltetradecane, 2,6,10-trimethyldodecane, 2,3,10-trimethylundecane, 6-propyl dodecane, the linear paraffins C_nH_{2n+2} with $n \geq 14$;
- nitro methane, nitro ethane, nitro propane, nitrobenzene, nitro toluene;
- tert-butyl peroxide;
- diethyl carbonate;
- polyethoxyethylal;
- dimethoxymethane, diethoxypropane, diethoxybutane, di-n-pentylether, di-n-pentoxymethane;
- octanol, nonanol, dodecanol;
- dimethylglycol, dimethyldiglycol, ethyldiglycol, ethyltriglycol; and
- butyl glycol acetate,

in proportions chosen according to the boiling point and cetane number of each of the compounds employed.

7. Fuel formulation according to any one of claims 5 and 6, characterised in that the combination of components comprises proportions a, b, c and d of at least one compound selected from each of columns I, II, III and IV of the following matrix:

Cetane range	40 – 45	45 – 50	50 – 55	> 55
Distillation range (°C)	(I)	(II)	(III)	(IV)
50 – 100	1	2	3	4
100 – 150	5	6	7	8
150 – 200	9	10	11	12
200 – 250	13	14	15	16
> 250	17	18	19	20

wherein each compound from 1 to 20 is selected from compounds having a boiling point in the distillation range indicated and a cetane number in the cetane range indicated.

8. Fuel formulation according to claim 7, characterised in that in its composition the proportions a, b, c and d of each compound introduced into the combination is from 0 to 50% by volume.

9. Fuel formulation according to claim 7 or 8, characterised in that its composition is represented by the formula

$$B_{100-(a+b+c+d)}I_aII_bIII_cIV_d$$

wherein I, II, III, IV, a, b, c and d are defined as in claim 3.

10. Fuel formulation according to any one of claims 7 to 9, characterised in that in the MAID matrix,

- the component 1 is 2-methylhexane
- the component 2 is dimethylglycol or n-heptane
- the component 3 is dimethoxymethane
- the component 4 is nitro methane;
- the component 5 is diethyl carbonate or 2-methylheptane;

- the component 6 is 2-methyl octane;
- the component 7 is 2-methyl nonane;
- the component 8 is diethoxy propane diethoxy butane, nitro ethane, nitro propane or n-octane ;
- the component 9 is octanol, butyl glycol acetate or 3,6-dimethyl octane;
- the component 10 is 3-methyl nonane;
- the component 11 is 2,9-dimethyl-5,6-diisoamyl decane;
- the component 12 is di-n-pentyl ether, dimethyl diglycol, nonane, decane or undecane;
- the component 13 is ethyl diglycol;
- the component 14 is 3-ethyl decane
- the component 15 is 5-butyl nonane;
- the component 16 is. nonanol, di-n-pentoxymethane, nitrobenzene or nitro toluene;
- the component 17 is 7,8-dimethyl tetradecane or 2,6,10 trimethyl dodecane;
- the component 18 is 2,3,10-trimethyl undecane;
- the component 19 is 6-propyl dodecane; and
- the component 20 is dodecanol, ethyl triglycol, a mixture of linear paraffins C_nH_{2n+2} , $n \geq 14$) or polyethoxy ethylal.

11. Fuel formulation according to any one of claims 7 to 10, characterised in that the compounds introduced into the combination are selected by following a substantially diagonal direction extending from the top left towards the bottom right of the said MAID matrix.

12. Fuel formulation according to claim 11, characterised in that the said combination is produced with a representative of each line of the said MAID matrix.

13. Fuel formulation according to any one of claims 7 to 12, characterised in that its composition is represented by one of the formulas:

- $B_{30}1_{10}5_{10}15_{25}20_{25}$
- $B_{60}1_{50}6_{10}10_{10}15_{10}20_5$ and
- $B_{70}1_{10}15_{10}20_{10}$.

14. Operation method for an internal combustion engine, characterised in that it comprises supplying the said engine by means of a fuel formulation prepared by a method according to any one of claims 1 to 4 or defined in any one of claims 5 to 13.

15. Method according to claim 14, characterised in that the said internal combustion engine is developed for the HCCI combustion mode.